

# **Enhanced fluorescence of selected cationic dyes adsorbed on reduced charge montmorillonite**

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**ABSTRACT:** The aggregation of three cationic dyes (CD), crystal violet (CV), Nile blue (NB) and rhodamine B (RB) in aqueous solution was studied by Vis absorption spectrophotometry and compared with methylene blue (MB). The distribution of the dye species (monomers, dimers, trimers, and tetramers) in aqueous solutions with different concentrations of dye was calculated using equilibrium stepwise aggregation constants  $K_n$ . These cationic dyes were intercalated into montmorillonite (SAz-1) and its reduced charge form (RC-SA(210)) prepared by heating lithium montmorillonite (Li/SAz-1) at 210 °C. The fluorescence of fully saturated CD/SAz and low CD loaded CD/RC-SA(210) complexes was studied. Vis absorption spectra of CD aqueous solutions and Vis absorption spectra and X-ray diffraction

pattern ( $d_{001}$ ) of the CD/SAz and CD/RC-SA(210) solid complexes were obtained and evaluated. Huge fluorescence intensity was found for CV/RC-SA(210) and NB/RC-SA(210) complexes similarly as with the complex of methylene blue with reduced charge montmorillonite MB/RCM(210) described previously.

**KEYWORDS:** cationic dye, reduced charge montmorillonite, fluorescence.

## INTRODUCTION

The cationic dyes (CD) methylene blue, crystal violet, Nile blue and rhodamine B form aggregates in concentrated aqueous solutions (Klika, 1979; Stork *et al.*, 1972; Stůžka & Hanůš, 1980; Selwyn & Steinfeld, 1972) and/or at the interface of cationic dye/clay mineral surface (Klika *et al.*, 2004; 2007; Yariv & Nasser, 1990). Two main types of dye aggregation can be observed, i.e. H-aggregates with head-to-head orientation and less frequent J-aggregates with head-to-tail orientation (Bujdák, 2006). A degree of aggregation of some CD (e.g. methylene blue, crystal violet, Nile blue) relates to dimers, trimers, tetramers and probably even higher polymers. Formation of the dye aggregates on clay mineral surface was described by Bergmann and O'Konski (1963) already more than 40 years ago. This interaction is related to colour change called metachromasy, a replacement of principal band of dye monomers in the visible region by band at a shorter

(related to H-aggregates) and/or longer (related to J-aggregates) wavelengths. The aggregation of dye in aqueous solution is influenced by concentration and type of dye (Klika, 1979; Stork *et al.*, 1972; Stůžka & Hanuř, 1980; Selwyn & Steinfeld, 1972), while in aqueous dispersion with clay mineral the dye aggregation runs in larger extent and it is influenced also by its layer charge (Czimerov *et al.*, 2006).

The layer charge is a very important parameter of clay minerals determining their physical and chemical properties. The term “layer charge” includes both permanent and variable charge of clay mineral (Czimerov *et al.*, 2006). The permanent charge arises from non-equivalent isomorphic substitution of the central atoms in octahedral and/or tetrahedral sheets. The variable, i.e. pH dependent charge occurs at specific functional groups (especially hydroxyl groups) on montmorillonite edges. These groups exhibit acid/base character. In smectites, the permanent charge is significantly higher than variable charge, and is compensated by exchangeable cations (e.g. Na<sup>+</sup>, Ca<sup>2+</sup>). The charge density in original smectites is so high, that common cationic organic dyes are heavily aggregated after complete exchanging small inorganic cations. To avoid this aggregation, the permanent charge can be reduced by Hofmann-Klemen effect (Hofmann & Klemen, 1950) – heating the clay mineral at 200-300 °C after their exchange with small ionic radius, e.g. Li<sup>+</sup> that causes migration of the small dehydrated cations into pseudohexagonal holes of tetrahedral

layers and vacant octahedral positions and consequently reduces the ion-exchangeable layer charge (Komadel *et al.*, 2005; Alvero *et al.*, 1994). The extent of charge reduction depends on ion radius of intercalated cation, chemical composition of clay mineral, temperature and time of the heating (Madejová, 2005; Su & Shen, 2005).

Many studies (e.g. Klika *et al.*, 2004; Bujdák *et al.*, 2001; 2002; Dobrogowska *et al.*, 1991) have shown that the density of negative layer charge and/or dye concentration influence substantially the aggregation of intercalated dye. The clay minerals with high density of layer charge support the aggregation because of short distances between neighbouring adsorbed dye cations on clay surface; oppositely, low charge density of clay mineral limits the contact between neighbouring adsorbed dye cations and hence suppresses the dye aggregation (Bujdák *et al.*, 1998).

The dye aggregation, the amount of dye (Endo *et al.*, 1986; 1988; Klika *et al.*, 2009) and orientation of dye molecules adsorbed on the surface (Sasai *et al.*, 2004; Salleres *et al.*, 2009) and/or in the structure of clay mineral (Villemure *et al.*, 1986) influence the fluorescence of dye/clay mineral complexes. For example fluorescence band of fully saturated montmorillonite with methylene blue (MB) is wide and has a very low intensity. This intensity can be further decreased if the charge of montmorillonite is higher and more MB is inserted in the interlayer space (Klika *et al.*, 2007). It is in agreement with Endo *et al.* (1988) who reported

the fluorescence quenching due to the increasing amount of intercalated dye. The low fluorescence was recorded also for methyl red adsorbed on montmorillonite and vermiculite (Martynková *et al.*, 2008) and for tetracationic porphyrin intercalated into the thin film of three smectites with high (fluorohectorite), medium (montmorillonite) and low layer charge (laponite) (Čeklovský *et al.*, 2008). All these dye/clay complexes were probably prepared at full saturation of the clay minerals by dyes. Intercalation of CD from more concentrated aqueous solutions into clays results in the formation of dye J- and/or H-aggregates (Sasai *et al.*, 2004). Whereas less frequent J-aggregates exhibit the fluorescence, the H-aggregation quenches the fluorescence (Sasai *et al.*, 2004; Salleres *et al.*, 2009). Also iron present in clay mineral structure is an effective fluorescence quencher (Klika *et al.*, 2009; Villemure *et al.*, 1986).

Recently Klika *et al.* (2009) have confirmed that the layer charge of montmorillonite, concentration of MB in aqueous solution and low MB loading considerably influence the fluorescence of MB/montmorillonite complexes. The authors concluded that the reduced charge of montmorillonite RCM(210) with low loading of MB has huge fluorescence intensity after laser excitation (Klika *et al.*, 2009). The fluorescence band of these complexes has a single sharp maximum, which matches to presence of dye monomers bonded on the montmorillonite surface.

The aim of this paper is to check whether the reduced loading of dye enhances significantly the fluorescence of further dyes with different spectral properties. For this purpose RCM(210) complexes with other CD (crystal violet, Nile blue and rhodamine B) have been studied.

## MATERIALS AND METHODS

### *Samples and chemicals*

Ca-montmorillonite (SAz-1) from Arizona (USA) was used as host for the saturation with cationic dyes. The SAz-1 (denoted here as SAz) was supplied by Source Clays (The Clay Minerals Society, Purdue University, IN, USA). The fraction with grain size below 4.5  $\mu\text{m}$  was prepared from the original montmorillonite sample (M) by sedimentation and subsequent air-drying. The cation exchange capacity (CEC) of SAz is 1.40  $\text{meq.g}^{-1}$  and specific surface area 93  $\text{m}^2.\text{g}^{-1}$ .

Four cationic dyes methylene blue (MB), crystal violet (CV), Nile blue (NB) and rhodamine B (RB), all supplied by Fluka, were used for the preparation of CD/montmorillonite complexes. CD formulas are shown in Figs. 1-4. The dyes were dissolved in distilled water, re-crystallized and dried under vacuum to constant mass. The solutions of CD for montmorillonite intercalation were prepared by dilution of the  $5 \times 10^{-3} \text{ mol dm}^{-3}$  CD solution with distilled water. Precise concentrations of the dyes solutions were determined spectroscopically.

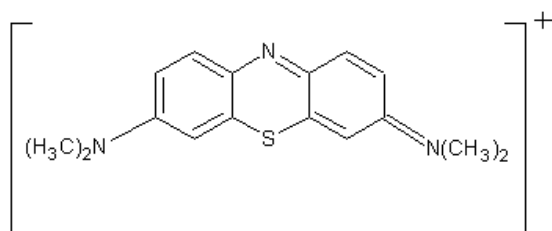


FIG. 1. Cation of methylene blue (MB).

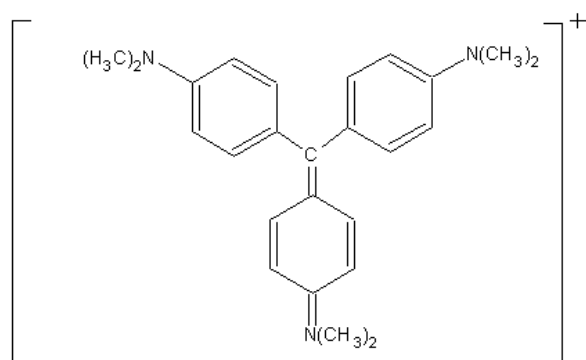


FIG. 2. Cation of crystal violet (CV).

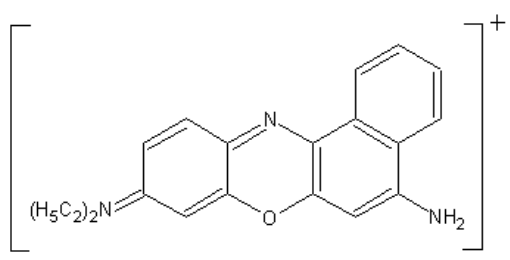


FIG. 3. Cation of Nile blue (NB).

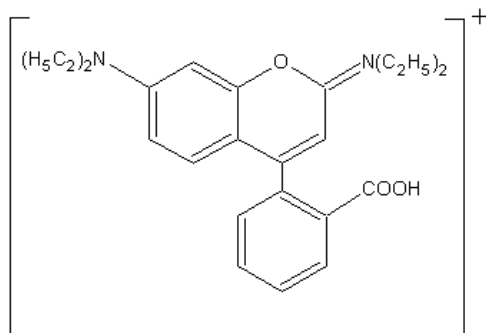


FIG. 4. Cation of rhodamine B (RB).

#### *Instruments and methods*

Absorption spectra of CD in aqueous solutions were recorded by UV-Vis spectrophotometer (Lambda 25, Perkin Elmer) using glass cells of 0.01 to 5 cm thickness at wavelength range 400 – 800 nm.

For the fluorescence measurements the powder samples were placed on the quartz substrates. The fluorescence was excited using a CW He-Cd laser at 325 nm. The 1 mW laser beam was focused by a 10 cm lens onto the front side of the sample; the fluorescence light was collected under 45° geometry and focused on the entrance slit of the grating spectrograph with a CCD. The spectral resolution of the apparatus was about 0.5 nm. The measurements were done at room temperatures ( $20 \pm 2$  °C).

The Vis electronic spectra of CD/montmorillonite complexes in solid state were recorded by diffuse reflectance spectra (DRS) method using a spectrometer (Perkin Elmer Lambda 35) equipped with an integrating sphere (Labsphere). The spectra of the montmorillonite powders were



measured in circular cells with quartz windows between 400 - 900 nm with a 0.5 nm step.

The X-ray diffraction patterns were recorded by Bruker D8 Advance diffractometer (Bruker AXS, Germany) equipped with fast position sensitive detector VÅNTEC 1 under following conditions: the reflection mode, rotating sample holder and  $\text{CoK}\alpha$  irradiation.  $\text{LaB}_6$  was used as a calibration standard. Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data).

BET surface area measurements were performed on the Sorptomatic 1990 (Thermo-Finnigan) using adsorption of  $\text{N}_2$  at 77 K. The residual moisture and adsorbed gases on the sample were removed by vacuum pump before measurement.

Cation exchange capacity of the montmorillonite samples was determined using the ion exchange reaction with barium chloride solutions (Czímerová *et al.*, 2006). Concentrations of excess barium cations after equilibration were determined by atomic absorption spectrometry (Varian AA280FS).

#### *Preparation of reduced charge montmorillonite*

The 1 g of SAz portion (sample 1) was used to prepare the reduced charge montmorillonite (RC-SAz). This portion was shaken with 100 cm<sup>3</sup> of  $\text{LiNO}_3$  solution (1 mol dm<sup>-3</sup>) at  $20 \pm 2$  °C for 2 hours at 200 oscillations per

minute in the polypropylene vessel. Then solid/liquid phases were separated by centrifugation for 20 min at 4500 rpm. The solid sample was repeatedly shaken with fresh  $\text{LiNO}_3$  solution in order to get Li homoionic form of SAz. The sample was washed with distilled water to remove nitrate ions and dried in vacuum. The reduced charge montmorillonite (RC-SA<sub>z</sub>(210); sample 6) was then prepared by heating of fully saturated Li/SA<sub>z</sub> at 210 °C for 24 hours (Bujdák *et al.*, 2002; Bujdák & Komadel, 1997). The cation exchange capacity (CEC) and specific surface area of RC-SA<sub>z</sub>(210) were determined and they are 0.10 meq.g<sup>-1</sup> and 117 m<sup>2</sup>.g<sup>-1</sup>, respectively.

#### *Preparation of CD complexes with SA<sub>z</sub> and RC-SA<sub>z</sub>(210)*

Ca-montmorillonite (SA<sub>z</sub>) and reduced charge montmorillonite heated at 210 °C (RC-SA<sub>z</sub>(210)) were treated with selected cationic dyes.

0.2 g of SA<sub>z</sub> sample was added to 100 cm<sup>3</sup> of  $5 \times 10^{-3}$  mol dm<sup>-3</sup> CD solution in a polypropylene vessel. The dispersion was shaken at  $20 \pm 2$  °C for 20 minutes at 200 oscillations per minute. Then solid and liquid phases were separated by centrifugation for 20 min at 4500 rpm. The solid sample was repeatedly shaken with fresh CD solution to get of fully saturated CD/SA<sub>z</sub> sample. The solid was washed with distilled water and dried in vacuum (samples 2-5).

0.2 g of RC-SA<sub>z</sub>(210) portion was added to 4 cm<sup>3</sup> of  $5 \times 10^{-4}$  mol dm<sup>-3</sup> CD solution in a polypropylene vessel. The dispersion was shaken at

20  $\pm$  2 °C for 20 minutes at 200 oscillations per minute and then centrifugation for 20 min at 4500 rpm was performed. The CD/SAz(210) sample was washed with distilled water and dried in vacuum (samples 7-10).

The labelling of the prepared montmorillonite samples is shown in

TABLE 1. The CD/montmorillonite complexes.

Sample	Treatment of montmorillonite	Labelling
1	Montmorillonite SAz-1	SAz
2	Montmorillonite fully saturated with MB ( $5 \times 10^{-3}$ mol dm $^{-3}$ )	MB/SAz
3	Montmorillonite fully saturated with CV ( $5 \times 10^{-3}$ mol dm $^{-3}$ )	CV/SAz
4	Montmorillonite fully saturated with NB ( $5 \times 10^{-3}$ mol dm $^{-3}$ )	NB/SAz
5	Montmorillonite fully saturated with RB ( $5 \times 10^{-3}$ mol dm $^{-3}$ )	RB/SAz
6	RC-SAaz prepared from Li/SAz at 210 °C	RC-SAaz(210)
7	RC-SAaz(210) with 10 % MB loading ( $5 \times 10^{-4}$ mol dm $^{-3}$ )	MB/RC-SAaz(210)
8	RC-SAaz(210) with 10 % CV loading ( $5 \times 10^{-4}$ mol dm $^{-3}$ )	CV/RC-SAaz(210)
9	RC-SAaz(210) with 10 % NB loading ( $5 \times 10^{-4}$ mol dm $^{-3}$ )	NB/RC-SAaz(210)
10	RC-SAaz(210) with 10 % RB loading ( $5 \times 10^{-4}$ mol dm $^{-3}$ )	RB/RC-SAaz(210)

*Notes.* Samples 2-5 were saturated with  $5 \times 10^{-3}$  mol dm $^{-3}$  CD, samples 7-10 with  $5 \times 10^{-4}$  mol dm $^{-3}$  CD. Percentages of CD loading in samples 7-10 are related to sample 6.

## RESULTS AND DISCUSSION

### *Vis absorption spectra of cationic dyes in aqueous solution*

The cationic dyes (CD) aggregate in aqueous solution; in the more concentrated dye solutions the higher aggregates occur (Klika, 1979; Stork *et al.*, 1972; Stučka & Hanuš, 1980; Selwyn & Steinfeld, 1972). Except for rhodamine B (RB), which forms only dimers, all other studied dyes are also trimeric and probably even higher polymeric. The Vis absorption spectra of the cationic dyes are shown in Figs. 5A-D. The monomers of methylene blue (MB) have absorption maximum centred at 664 nm, the dimers at 605 nm and the higher aggregates at even lower wavelengths (Fig. 5A). The absorption maximum of the monomers of crystal violet (CV) is centred at 590 nm, the dimers at 550 nm and higher aggregates at about 540 nm (Fig. 5B). The absorption spectra of Nile blue (NB) are shown in Fig. 5C. Similarly as for previous dyes, the wavelength of absorption bands of NB decreases with increasing aggregation (monomers 641 nm; dimers 597 nm; higher aggregates about 574 nm). The aggregation of Nile blue is the highest from all presented CDs (Fig. 5). This observation is in agreement with the report by Stučka & Hanuš (1980). They confirmed the formation of NB higher aggregates in aqueous solutions with concentration higher than  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ .

The aggregation of RB (monomers 554 nm; dimers 524 nm) and the isobestic point (530 nm) in Vis absorption spectra are shown in Fig. 5D.

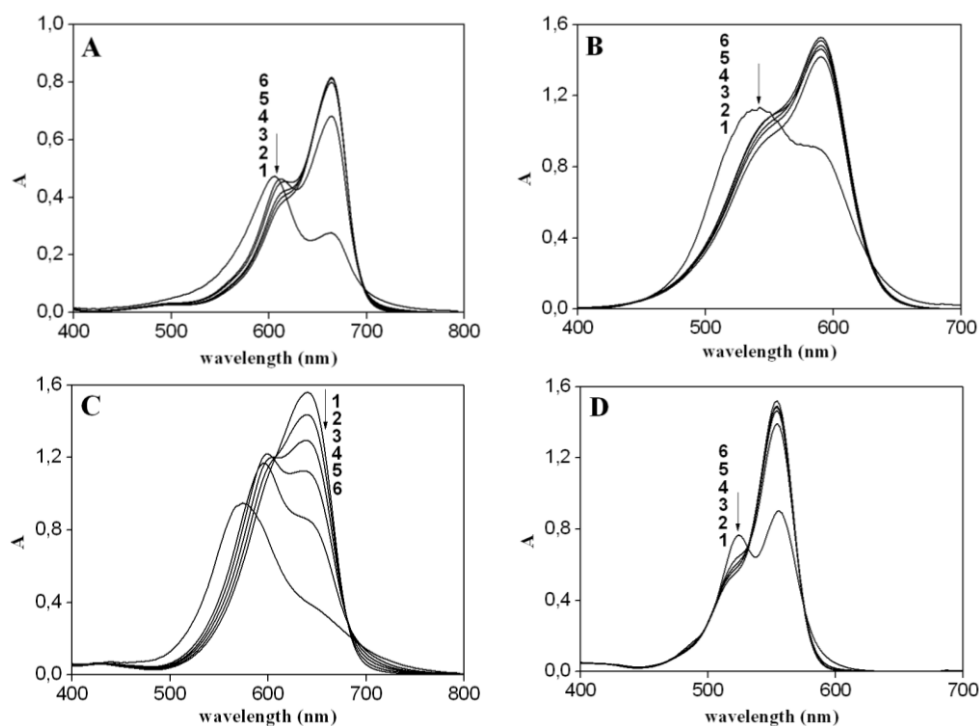
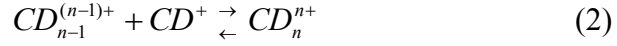


FIG. 5. Vis absorption spectra of cationic dyes in aqueous solution. A, Methylene blue; B, Crystal violet; C, Nile blue; D, Rhodamine B.

spectrum 1 -  $3.0 \times 10^{-6} \text{ mol dm}^{-3}$ , (5 cm cell); spectrum 2 -  $7.5 \times 10^{-6} \text{ mol dm}^{-3}$ , (2 cm cell); spectrum 3 -  $1.5 \times 10^{-5} \text{ mol dm}^{-3}$ , (1 cm cell); spectrum 4 -  $3.0 \times 10^{-5} \text{ mol dm}^{-3}$ , (0.5 cm cell); spectrum 5 -  $7.5 \times 10^{-5} \text{ mol dm}^{-3}$ , (0.2 cm cell); spectrum 6 -  $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ , (0.01 cm cell).

#### *Aggregation of cationic dyes in aqueous solution*

The aggregation of cationic dyes (CD) in aqueous solution can be described by total (Eq. 1) or by stepwise (Eq. 2) chemical reactions:



where  $n$  is the number of  $CD^+$  monomers or the  $n$ -th CD aggregate. The equilibriums of Eq. (1) and Eq. (2) are given by Eq. (3) and (4), respectively.

$$\beta_n = \frac{[CD_n^{n+}]}{[CD^+]^n} \quad (3)$$

$$K_n = \frac{[CD_n^{n+}]}{[CD_{n-1}^{(n-1)+}] \cdot [CD^+]} \quad (4)$$

where  $\beta_n$  is total and  $K_n$  stepwise equilibrium aggregation constants. The relations between  $\beta_n$  and  $K_n$  are as follows:

$$\beta_2 = K_2; \quad \beta_3 = K_2 \cdot K_3; \quad \beta_4 = K_2 \cdot K_3 \cdot K_4;$$

The total analytical concentration of cationic dye ( $c_{CD}$ ) is then given by Eq. 5 as sum of equilibrium concentrations of not aggregated and aggregated CD species.

$$c_{CD} = \sum_{n=1}^4 n \cdot [CD_n^{n+}] \quad (5)$$

The stepwise aggregation constants of MB, CV, NB and RB determined earlier are given in Table 2. As it has been demonstrated above the NB aggregation is the biggest of all here studied CD but Stuzka & Hanuš (1980) determined only  $K_2$  aggregation constant for the formation of NB dimers. Therefore a parameter model X (Ghosh & Mukerjee, 1970) for the

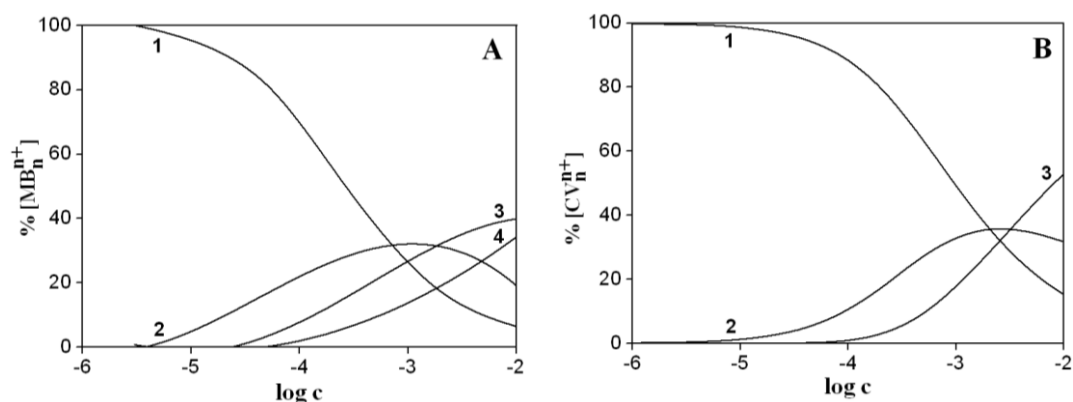
calculation of higher NB aggregation constants  $K_3$  and  $K_4$  and arithmetic mean of  $K_2$  data of Stučka & Hanuš (1980) were used. These calculated constants are given in parentheses in Table 2.

TABLE 2. The stepwise aggregation constants for used cationic dyes.

Cationic dye	$K_2$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$K_3$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$K_4$ ( $\text{dm}^3 \text{mol}^{-1}$ )	Source
MB	$2.54 \times 10^3$	$1.35 \times 10^3$	$2.06 \times 10^2$	Klika, 1979
	$2.09 \times 10^3$	$4.00 \times 10^3$	$3.00 \times 10^3$	Ghosh & Mukerjee, 1970
CV	$6.80 \times 10^2$	$7.30 \times 10^2$		Lueck <i>et al.</i> , 1992
NM	$2.34 \times 10^5$	( $2.34 \times 10^5$ )	( $2.34 \times 10^5$ )	Stučka & Hanuš, 1980
RB	$1.43 \times 10^3$			Klika <i>et al.</i> , 2004

The percentages of CD species for different concentrations of CD in aqueous solution have been calculated using Eqs. (3), (4) and (5) and aggregation constants (Table 2). The arithmetic mean of stepwise aggregation constants of Klika (1979) and Ghosh & Mukerjee (1970) were used to calculate MB distribution. The calculated data are plotted in Figs.

6A-D.



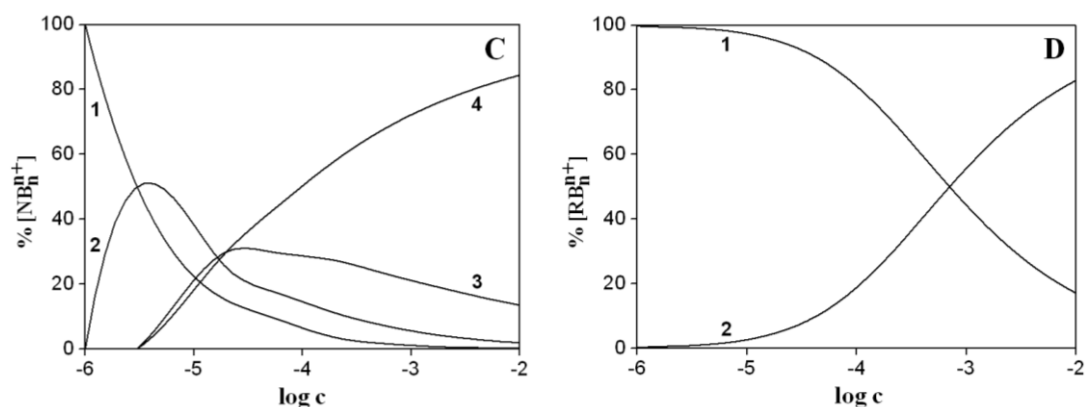


FIG. 6. Percentages of CD aggregates in aqueous solution for different analytical concentrations of CD ( $c$ ; in  $\text{mol dm}^{-3}$ ). A, methylene blue; B, crystal violet; C, Nile blue; D, rhodamine B.

The distributions of MB and CV monomers, dimers and trimers are very similar (Figs. 6A and 6B). The first formation of dimers appears at about  $3 \times 10^{-6} \text{ mol dm}^{-3}$  CD and trimers at about  $2\text{--}5 \times 10^{-5} \text{ mol dm}^{-3}$  CD. The aggregation of MB is more extensive and therefore also MB tetramers are formed.

As it has been already mentioned above that NB aggregation is the highest from all presented CDs (see also Fig. 6C). The formation of NB dimers can be observed already at  $1 \times 10^{-6} \text{ mol dm}^{-3}$  and its trimers and tetramers already at  $3 \times 10^{-6} \text{ mol dm}^{-3}$  NB; 50% tetramers appears already in NB aqueous solution with analytical concentration of  $1 \times 10^{-4} \text{ mol dm}^{-3}$  NB.

RB has the simplest distribution of species forming only monomers and dimers (Fig. 6D).



### Fluorescence spectra

Recently Klika *et al.* (2009) has discovered that complexes of reduced charge montmorillonite with low methylene blue loading have huge fluorescence intensity after 325 nm laser excitation. To verify whether also other CDs have similarly huge fluorescence, new experiments were performed. For this study the CD/RC-SA<sub>z</sub>(210) complexes with 10% CD loading using  $5 \times 10^{-4} \text{ mol dm}^{-3}$  CD solutions were prepared. Reference CD/SA<sub>z</sub> complexes (original SA<sub>z</sub> fully saturated by  $5 \times 10^{-3} \text{ mol dm}^{-3}$  cationic dye) were used for comparison. The fluorescence spectra of all complexes are shown in Figs. 7A-D.

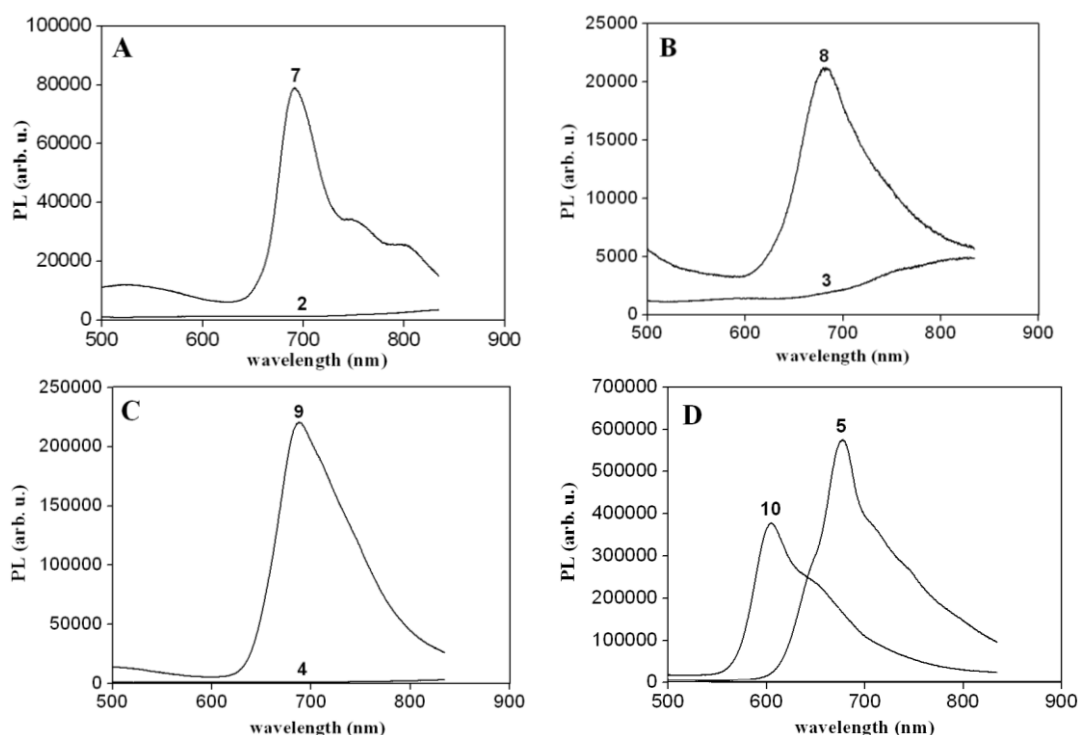


FIG. 7. Fluorescence spectra of CD/SAz (samples 2, 3, 4 and 5) and fluorescence spectra of CD/RC-SA<sub>z</sub>(210) (samples 7, 8, 9 and 10). A, Methylene blue; B, Crystal violet; C, Nile blue; D, Rhodamine B.

The fluorescence intensities of fully saturated CD/SA<sub>z</sub> complexes by methylene blue, crystal violet and Nile blue (spectra of samples 2, 3 and 4 in Figs. 7A, B and C, respectively) are very low. It is due to strong aggregation of the cationic dyes in more concentrated aqueous solution (see Figs. 5A-C). The aggregation of CD is known to effectively quench the fluorescence (Endo *et al.*, 1988; Klika *et al.*, 2009). In contrast to spectra 2, 3 and 4 the fluorescence spectrum of sample 5 in Fig. 7D shows very high intensity; it is because the RB is fluorescence cationic dye by itself (Klika *et al.*, 2004). Also imperfect, twisted dimer sandwiches with the distortion angle higher than 55° could exhibit intensive fluorescence band with maximum at longer wavelength than the monomer band as it was demonstrated by Sasai *et al.* (2004) for rhodamine 6G/montmorillonite complex.

The aggregation of dyes is suppressed by their deposition on montmorillonite with reduced layer charge RC-SA<sub>z</sub>(210) and by low (10%) CD loading (Klika *et al.*, 2009). That is why the fluorescence intensity of the CD/RC-SA<sub>z</sub>(210) complexes (spectra of samples 7, 8 and 9 in Figs. 7A, B and C, respectively) increases after laser excitation by several orders of magnitude. The maximal wavelength of these spectra (samples 7, 8 and 9)

varies from 680 to 700 nm. The fluorescence intensity of RB/RC-SAz(210) complex (spectrum of sample 10, Fig. 7D) is lower than that of fully saturated RB/SAz complex (spectrum of sample 5). There is also a big difference between the maximal wavelengths of fluorescence bands for samples 5 and 10 (680 nm for RB/SAz and 610 nm for RB/RC-SAz(210)). As described above the intensive fluorescence band at 680 nm of RB/SAz complex (sample 5) could be due to the formation of imperfect sandwiches of RB dimers.

The maximum of fluorescence intensity could be somewhat different (higher) from those that were determined in this paper if the conditions of preparation (e.g. concentration of dye in saturated solution, dye loading) have changed.

#### *XRD data*

The structural layers of the montmorillonite, i.e. the basal spacing ( $d_{001}$ ) of SAz substantially expands at high CD loading (Fig. 8). The basal distance is 1.51 nm in the original SAz (sample 1), 1.80 nm in MB/SAz (sample 2), 2.08 nm in CV/SAz (sample 3), 1.68 nm in NB/SAz (sample 4), and 1.90 nm in RB/SAz (sample 5). The increase of the basal spacing is due to the intercalation of CD into the SAz interlayer. The basal spacing of the CV and RB complexes are larger because of a larger size of these CD molecules – they have as much as 3 dimethylamino groups (CV) and 2

diethylamino groups (RB) on the aromatic skeletons of similar size of all four CDs. The increase of the basal spacing of the intercalates shows that CDs are aggregated and/or tilted in the interlayer space.

The decrease of the original interlayer spacing ( $d_{001}$ ) of SAz (sample 1) from 1.51 nm to 0.96 nm of RC-SAz(210) (sample 6) is due to the reduction of SAz charge by Hofmann-Klemen effect (Hofmann & Klemen, 1950) which removes almost all hydrated interlayer cations from the original smectite. After the low CD loading and the formation of the CD/RC-SAz(210) complexes the interlayer spacings of samples 7-10 are very close to that of the parent smectite (sample 6) proving that CD has not been intercalated. It can be supposed that CDs in CD/RC-SAz(210) complexes (samples 7-10) are mainly adsorbed on the outer surface of RC-SAz(210) samples.

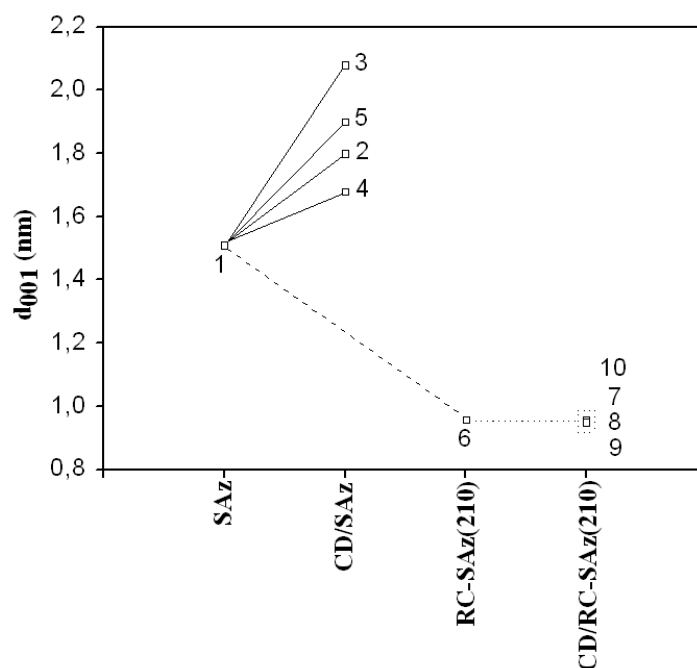


FIG. 8. Interlayer spacing ( $d_{001}$ ) of samples 1-10. (For samples see Table 1.)

#### *Vis electronic spectra*

The diffuse reflectance Vis spectroscopy was used to study of CD species in montmorillonite complexes. The recorded spectra of prepared complexes are given in Fig. 9. In Vis electronic spectra of fully saturated CD/SAz complexes H-aggregates (head-to-head association) prevail with maximal wavelength 526 nm for NB/SAz (spectrum 4), 520 nm for MB/SAz (spectrum 2) and 480 nm for complex CV/SAz (spectrum 3). The maximum of absorption bands of H-aggregates are shifted to shorter wavelength compared them with wavelengths of H-aggregates present in aqueous solution (see Fig. 5). The next absorption band of fully saturated CD/SAz complexes (spectra 2, 3 and 4) is broad and asymmetric with maximal wavelength at about 710 nm for NB/SAz (spectrum 4), 690 nm for MB/SAz (spectrum 2) and 650 nm for CV/SAz (spectrum 3). We suppose that they respond to dye monomers. In contrast to dye monomers present in aqueous solution they are shifted to longer wavelength. The bathochromic shift of monomeric band is induced by adsorption of dye into the interlayer space of montmorillonite (Yariv & Nasser, 1990; Cenens & Schoonheydt, 1988).

Vis electronic spectrum of RB/SAz complex (spectrum 5) has not very good distinguishable absorption maxima. Probably the absorption band

of dye monomer (about 560 nm) and band related to imperfect sandwiches of RB dimers (about 600 nm) could be distinguished.

In CD/RC-SAz(210) complexes (spectra 7, 8, 9 and 10) the monomer species prevail. The intensities of absorption bands as well as their number are both much lower in contrast to CD/SAz. The most prominent absorption bands of the solid complexes (Fig. 9) have maxima close to those of the dye monomers in aqueous solutions (Fig.5). The maximal absorption bands of the monomers in solid complexes are at wavelengths about 664 nm for MB/RC-SAz(210) (spectrum 7), 640 nm for NB/RC-SAz(210) (spectrum 9), 590 nm for CV/RC-SAz(210) (spectrum 8) and 560 nm for RB/RC-SAz(210) (spectrum 10).

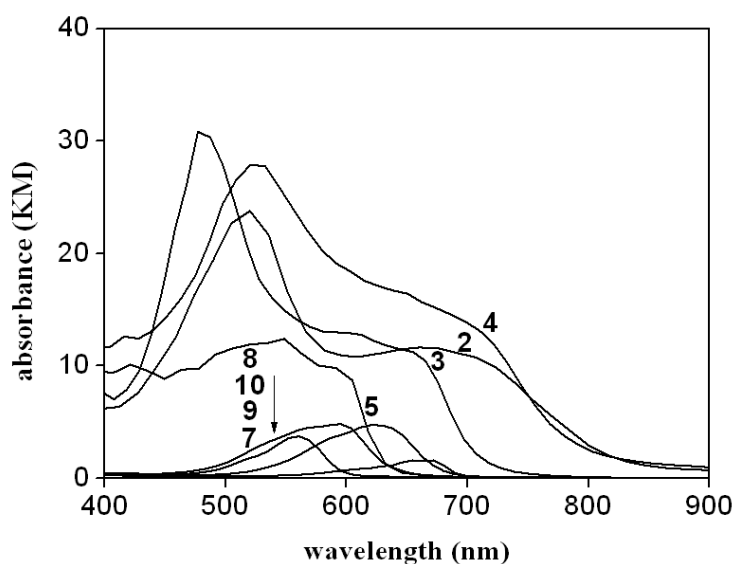


FIG. 9. Vis electronic spectra of solid state complexes of montmorillonite with cationic dye. (For samples see Table 1.)

## CONCLUSION

The fully saturated complexes of montmorillonite (SAz) with methylene blue, crystal violet and Nile blue have very poor fluorescence intensity due to the presence of CD higher aggregates in CD/SAz. As was shown before (Klika *et al.*, 2009) the fluorescence intensity increases by several orders of magnitude if methylene blue is sorbed on the reduced charge montmorillonite (MB/RCM(210)). In this paper it was shown that crystal violet and Nile blue behave similarly and their adsorption on the reduced charge montmorillonite substantially enhances the fluorescence. The explanations of this phenomenon are threefold:

a) the charge density of the reduced charge smectite decreases and simultaneously the interlayer distance decreases from 1.51 nm to 0.96 nm, which effectively closes the interlayer space for CD

b) low loading of the cationic dyes is on the outer surface of RC-SA(210), which decreases their intermolecular interactions, and

c) adsorbed dyes have parallel orientation with the outer surface of the smectite as it was shown by the molecular simulations of MB interactions with montmorillonites (Klika *et al.*, 2009).

The low loading of methylene blue, crystal violet and Nile blue on the external surface causes the prevalence of monomeric forms of the dyes, which was demonstrated by diffuse reflectance Vis spectroscopy.

In contrast to fully saturated complexes of montmorillonite (SAz) with methylene blue, crystal violet and Nile blue the fully saturated complexes of montmorillonite (SAz) with rhodamine B shows very high fluorescence intensity. It is due to the absence of rhodamine B higher aggregates and probably also due to the presence of imperfect, twisted sandwiches of rhodamine B dimers that probably do not quench fluorescence of prevailing dye monomers. This explanation is supported by observation of Sasai *et al.* (2004) that described imperfect, twisted sandwiches of rhodamine 6G dimers in rhodamine 6G/montmorillonite complex with high fluorescence.

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